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12

Fourier Transform Infrared Spectroscopic Study of Aging in Commercial Polyurethane

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Capt David Thyfault/YNSA was the project officer for the Mission-Oriented Investigation and Experimentation Program.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Satellite electronics systems may function for years before failing as a result of a shorted-out component. If the insulation is considered to be perfectly inert, then such failures would be inexplicable in terms of events intrinsic to the material. However, many physical and chemical changes may occur in the dielectric prior to breakdown. Hence, a polymer dielectric is not inert and may be more accurately thought of as a seething molecular and

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electronic cauldron, which gradually drifts in the direction of diminished resistance to applied electrical stress. After a time, which appears indefinite only because we have not adequately characterized the system, the constant electrical stress shorts out the degraded insulation. A correlation between decreases in infrared absorbance, molecular motion, electronic energy transfer, and increasing susceptibility to electric stress is supported by the data presented here. It is suggested that the development of new, voltage-stabilized materials can be greatly facilitated by using Fourier transform infrared spectroscopy (FTIR) as a diagnostic tool, and thermal aging as an accelerated aging test. Keywords:

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Satellite electronics systems may function for years before failing as a result of a shorted-out component. If the insulation is considered to be perfectly inert, then such failures would be inexplicable in terms of events intrinsic to the material. However, many physical and chemical changes may occur in the dielectric prior to breakdown. Hence, a polymer dielectric is not inert and may be more accurately thought of as a seething molecular and

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FIGURES

I. INTRODUCTION*

Ieda[1] has reviewed the wide range of physical processes that may occur in polymer dielectrics prior to breakdown. One facet of this microscopic world was monitored by Mitsui et al.,[2] who subjected microtomed specimens of electrically aged epoxy to Fourier transform infrared spectroscopy (FTIR) in order to monitor the epoxy's molecular state, which varied as if the cure were continuing. One of the goals of this report is to show the corresponding results for electrically aged polyurethane. In addition, physical, or shelf-life, aging effects discovered in the FTIR of polyurethanes are presented, because such effects must be discounted when evaluating purely electrical effects. Finally, thermal aging results will be presented. These results will be seen to be similar to the electrical aging results, thereby offering the possibility of accelerated testing of polyurethane and other polymeric dielectrics. The ultimate goal of this research is to develop a technique for testing new materials or formulations. It is anticipated that the demonstration of reduced molecular activity in pre-breakdown aging will likely predict the attainment of new, voltage-stabilized materials.

*This work appeared in the 1985 Annual Report of the Conference on Electrical Insulation and Dielectric Phenomena (IEEE Publications, Piscataway, N. J.), p. 371.

II. EXPERIMENTAL TECHNIQUE

In this study we chose the polyurethane Uralane 5753 from M & T Chemicals, Los Angeles. The polyol is hydroxy-terminated polybutadiene (PBD), and the isocyanate is 4,4'-diphenylmethane diisocyanate (MDI). Uralane specimens (1.5 mil nominal thickness) for transmission infrared analysis were microtomed from freshly prepared, 0.125-in.-thick slabs that had been subjected to physical, thermal, or electrical aging experiments. A Nicolet MX-1 FTIR with a Harrick 4× beam condenser was used for transmission measurements. Measurement times between 1 and 4 min were used to obtain suitable spectra at 2 cm^{-1} resolution. Reference spectra were collected prior to physical and thermal aging for the subsequent construction of difference spectra. The electrical-aging reference spectrum is described below.

Physical, or shelf-life, aging was conducted for 4 months at room temperature. Thermal aging occurred at 100°C for 1 hr. Finally, a Uralane slab was aged between parallel-plate electrodes for 3 months (at 24 kVdc). This 0.125-in. slab extended well beyond the electrode area, i.e., some of the material saw essentially zero electric field. Thus, purely physical aging could be discounted in the electrical aging test by using the spectrum of a nonfield region as the reference. The electrical aging was performed with both the sample and electrodes immersed in Fluorinert (a high dielectric-strength fluid) to prevent extraneous breakdowns.

III. EXPERIMENTAL RESULTS

A. VALIDATION OF TECHNIQUE

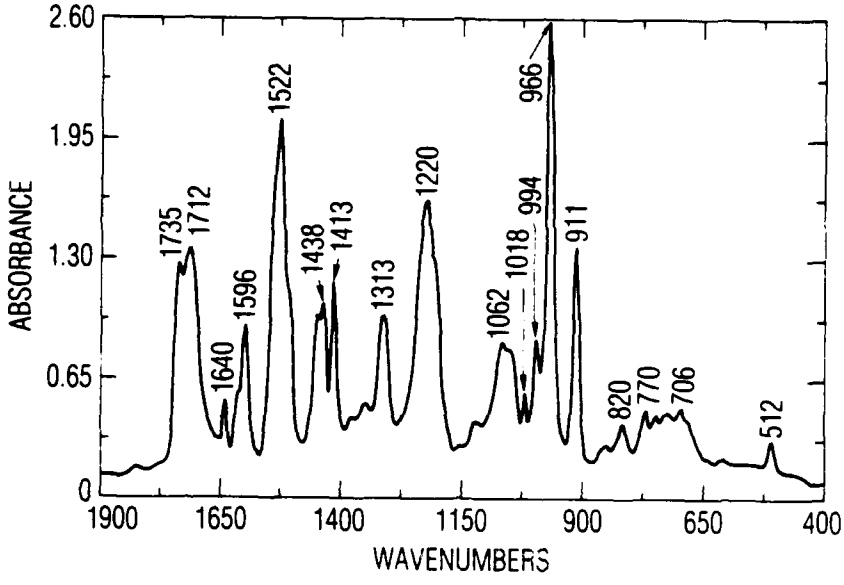
It is well known that saturation effects limit the usefulness of spectrometers.[3-8] Instrument line shape (ILS) problems give rise to unwanted effects in difference spectra. The subtraction of different Uralane spectra such as the ones shown in Fig. 1 could lead, in principle, to subtraction artifacts. However, we have measured these artifacts (compare Fig. 2 to Figs. 3 through 5, below), and know that they are less intense (and more random in sign) than the features we propose to interpret.

We microtomed specimens of different thicknesses from closely spaced regions of the same slab of the polyurethane PRC 1535, so that only sample-thickness effects are present. (This polyurethane is different from Uralane, but true ILS effects depend only on the band intensities, which are similar.) Specimens requiring FCR = 1 to 1.84 were investigated. (FCR is the spectral subtraction scaling factor on Nicolet instruments.)

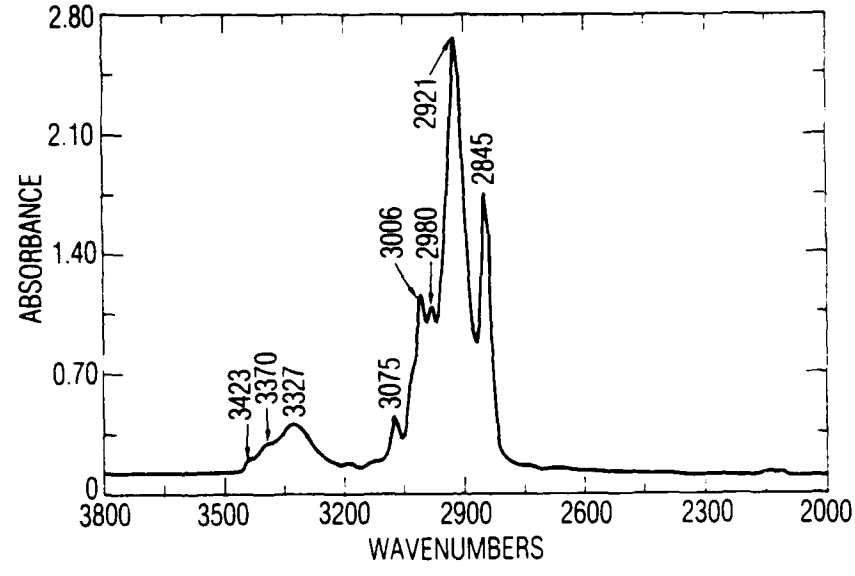
The worst-case (FCR = 1.84) artifacts are shown in Fig. 2. The top two spectra show maximum peak heights of around 2.3 and 1.3, which are typical of the Uralane specimens considered later. The bottom difference spectrum in Fig. 2 is the subtraction of the first two spectra and shows a maximum peak-to-peak undulation of about 0.12. This represents the maximum "unsubtractibility" for spectra having maximum peak heights of 2.3 and 1.3 (FCR = 1.84). From Fig. 4 it can be seen that the difference spectra peaks in an FCR = 1.8 plot are much bigger than this and are attributable to differences in the sample, not to the measurement technique. Similar results can be obtained for the smaller FCR values in Figs. 3 and 5.

B. PHYSICAL AGING

The FTIR difference spectrum of the 4-month-aged Uralane ("sample file") less the as-cast material ("reference file") is shown in Fig. 3. The "FCR number," or multiplier for the reference file prior to subtraction from the sample file, was selected by the following criteria: (1) the elimination or



A



B

Fig. 1. Uralane 5753 Survey Spectrum. (a) Lower frequencies. (b) Higher frequencies.

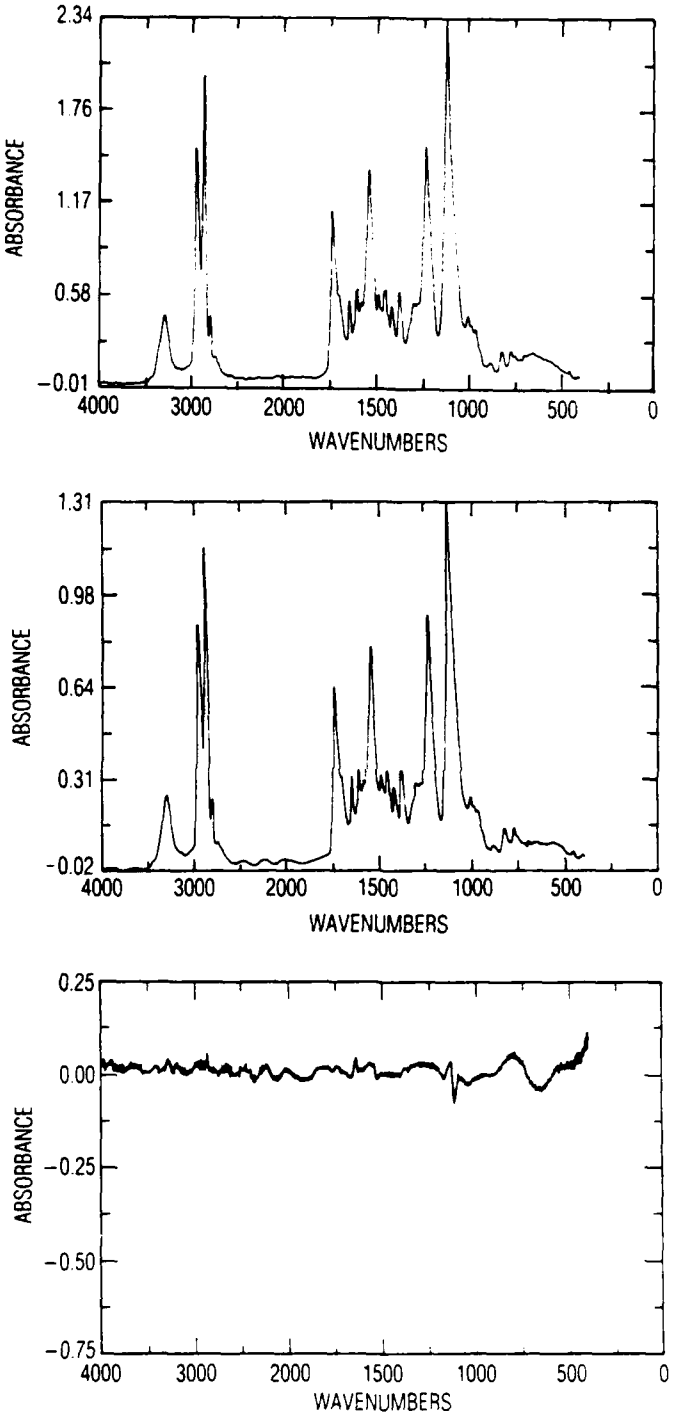


Fig. 2. Validation of Measurement Technique on PRC 1535 Samples Having Peak Absorbance Values Similar to Those of Uralane 5753. (FCR = 1.84 for the difference spectrum in the bottom graph.)

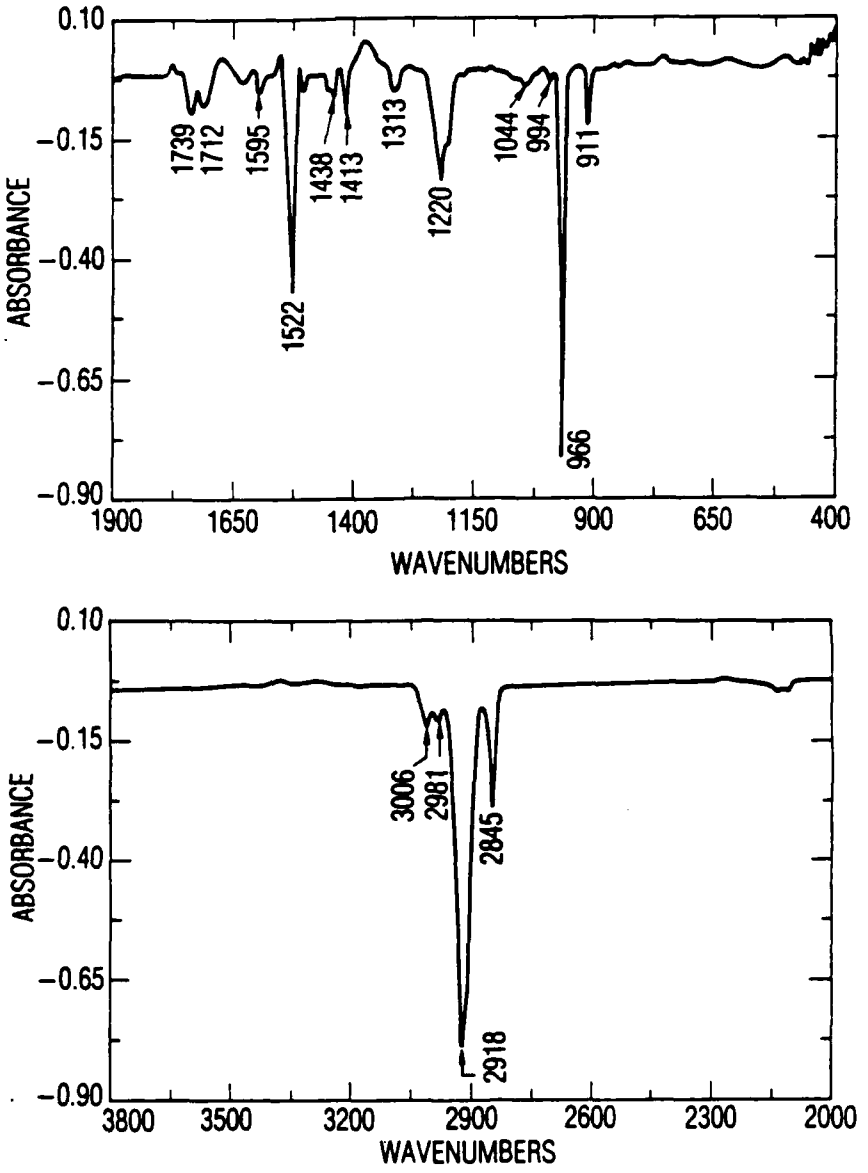


Fig. 3. Physical-Aging Difference Spectrum of Uralane 5753. (FCR = 1.14.)

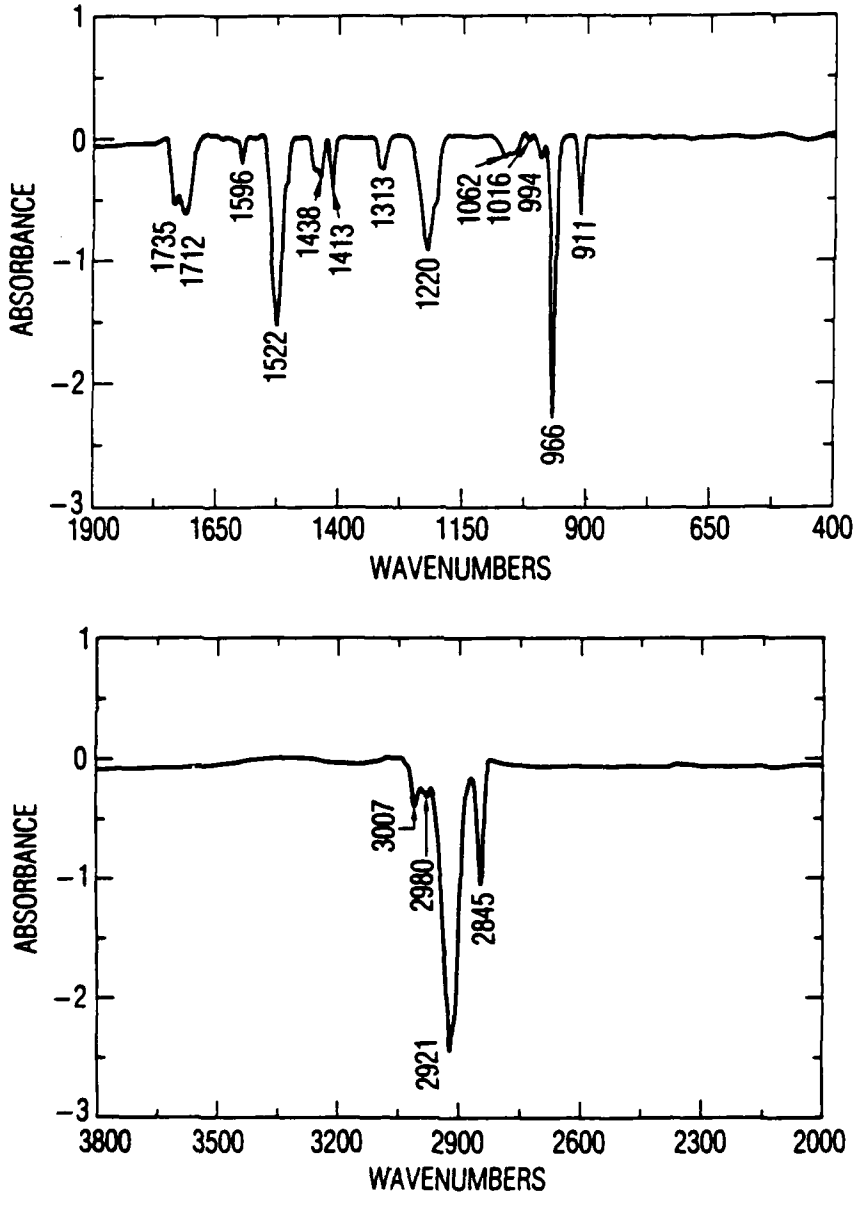


Fig. 4. Thermal-Aging Difference Spectrum of Uralane 5753. (FCR = 1.80.)

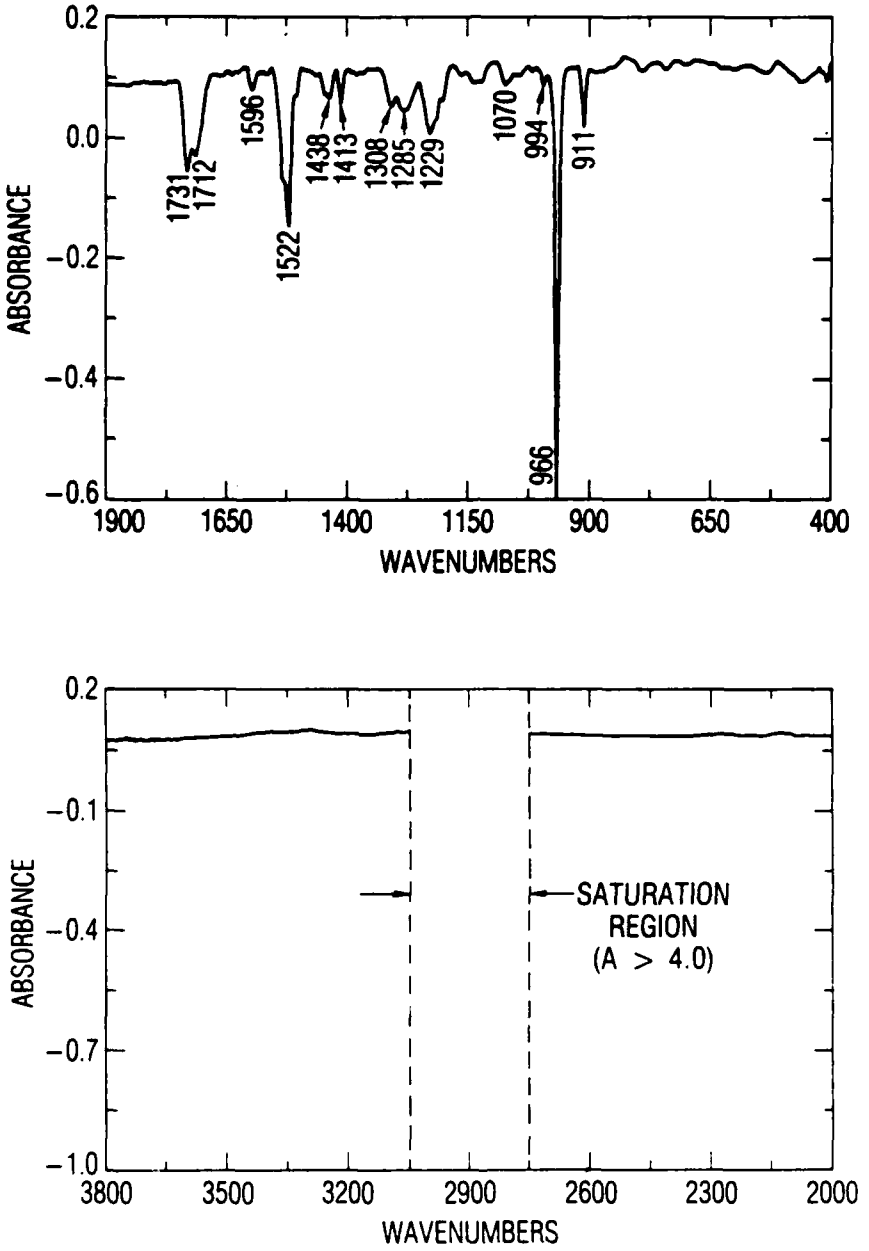


Fig. 5. Electrical-Aging Difference Spectrum of Uralane 5753. "A" refers to typical peak absorbance values. (FCR = 1.30.)

minimization of as many peaks in the difference spectrum as possible, and (2) the attainment of a flat and smooth baseline close to zero absorbance.

We believe that this selection algorithm is accurate, for the following reasons: (1) Flat and smooth baselines near zero absorbance are actually achieved. (2) Some bands do subtract out exactly to within experimental error. For example, all the bands below 900 cm^{-1} subtract out, as well as the 3450, 3400, 3310, and 3080 cm^{-1} bands. These bands are immediately adjacent to the 966, 2918, and 2850 cm^{-1} bands, which do decrease strongly. (3) The ratio of the absolute values of the strongest peak heights is different in the case of the survey spectrum and in the case of the difference spectrum. Thus, the difference spectrum does not arise merely as the result of "oversubtraction" (i.e., selection of a too-large FCR number).

C. THERMAL AGING

The FTIR difference spectrum of the 100°C, 1-hr-aged Uralane less the starting material is shown in Fig. 4. The spectral quality is judged to be excellent, for the reasons given above. In its main features this thermal-aging difference spectrum is very similar to the physical aging result, but is more intense. Thus thermal aging seems largely to be accelerated physical aging.

D. ELECTRICAL AGING

The difference spectrum of the electrically aged Uralane less the edge material, which had seen essentially zero electric field, is shown in Fig. 5. The purely physical aging effects are therefore subtracted out. The spectral quality is again seen to be excellent. Much the same spectral results as with physical and thermal aging are observed: below 900 cm^{-1} and above 3050 cm^{-1} the peaks subtract out exactly to within experimental error. These are some small, detailed differences in the 990 to 1200 cm^{-1} region and near 1280 cm^{-1}.

IV. DISCUSSION AND CONCLUSIONS

Beer's Law states that A = abc, where A, a, b, and c denote absorbance, activity, thickness, and concentration, respectively. An interpretation of the virtually uniformally negative-going, difference-spectra peaks in terms of changes of b or c seems counterintuitive.[9] It would seem more fruitful to interpret changes in A in terms of changes in a. There is a precedent for such changes, as discussed below.

It is expected that Uralane forms a phase-separated structure, since the PBD is nonpolar, while the urethane groups exhibit strong interchain interactions (hydrogen bonding). There is only a low level of order in such an as-polymerized system. Differential scanning calorimetry results, discussed in another report,[9] show that a paracrystallization process occurs upon heating. Thus there is a driving force for time- and temperature-dependent chain rearrangement in this system.

Changes in absorbance have long been associated with a changing intermolecular environment,[10] including molecular strain and ordering. Joss, Bretzlaff, and Wool[11] note that significant progress in the quantitative interpretation of infrared intensities has only recently become possible, in contrast to the long-standing success of the Wilson GF matrix analysis[12] of normal vibration frequencies. Intensity calculations for phase-separating systems would be very difficult, but it is not surprising that changes in infrared activity occur as the average molecular environment changes.

Consistent with this view, we have documented that observable FTIR changes occur during physical, thermal, and electrical aging of polyurethane prior to breakdown. The latter two types of aging seem to be accelerated physical aging, presumably due to the availability of extra energy inputs.

The mechanism for energy input in the case of electrical aging might start with the formation of free-volume holes or "grain boundaries." These would increase the energy transfer (via electron scattering) from the electric field to the imperfection sites. This would exacerbate gas formation and

speed the occurrence of breakdown. Thus, the authors believe that there is a significant correlation between infrared absorbance decreases, molecular motion, electronic energy transfer, and increasing susceptibility to electric stress.

Results of a recent work[13] indicate that FTIR spectroscopy, coupled with thermal aging, will greatly facilitate the development of new, voltage-stabilized materials.

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